(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 1 072 599 B1

(12) **EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention of the grant of the patent:
18.08.2004 Bulletin 2004/34

(51) Int Cl.[7]: **C07D 301/12**

(21) Application number: **00202657.3**

(22) Date of filing: **24.07.2000**

(54) **Process for the preparation of olefin oxides**

Verfahren zur Herstellung von Olefinoxiden

Procédé pour la préparation d'oxydes d'oléfine

(84) Designated Contracting States:
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU MC NL PT SE

(30) Priority: **27.07.1999 IT MI991657**

(43) Date of publication of application:
31.01.2001 Bulletin 2001/05

(73) Proprietor: **Dow Global Technologies Inc.**
Midland, Michigan 48674 (US)

(72) Inventors:
- **Paparatto, Giuseppe**
  20092 Cinisello Balsamo, Milan (IT)
- **Forlin, Anna**
  35010 Vigonza, Padova (IT)
- **Tegon, Paolo**
  30030 Oriago, Venezia (IT)

(74) Representative: **Raynor, John et al**
W.H. Beck, Greener & Co
7 Stone Buildings
Lincoln's Inn
London WC2A 3SZ (GB)

(56) References cited:
EP-A- 0 230 949
EP-A- 0 757 043
EP-A- 0 940 393
WO-A-00/17178

- **DATABASE WPI Section Ch, Week 200007 Derwent Publications Ltd., London, GB; Class E13, AN 2000-075359 XP002151674 & JP 11 309378 A (ASAHI KASEI KOGYO KK ET AL), 9 November 1999 (1999-11-09)**

EP 1 072 599 B1

Description

[0001] The present invention relates to a process in continuous for the preparation of olefin oxides.

[0002] More specifically, the present invention relates to a process in continuous for the preparation of propylene oxide by the direct epoxidation of propylene with hydrogen peroxide, or compounds capable of producing hydrogen peroxide under the reaction conditions, in a solvent medium, in the presence of a catalytic system consisting of a zeolite containing titanium and a nitrogenated organic base having formula (I).

[0003] Epoxides, or olefin oxides, are intermediates useful for the preparation of a wide variety of compounds. For example epoxides can be used for the production of glycols, condensation polymers such as polyesters, or for the preparation of intermediates useful in the synthesis of polyurethane foams, elastomers, seals and similar products.

[0004] It is known in literature that zeolitic compounds with an MFI structure containing titanium atoms (TS-1) are used as catalysts in the direct epoxidation reactions of olefin compounds with hydrogen peroxide (EP-100119).

[0005] However, the acidity which characterizes these catalysts, even if modest, is sufficient to catalyze consecutive solvolitic reactions on the epoxide with the opening of the ring. This leads to an increase in production costs for both the decrease in yield to epoxide and for the separation of the by-products formed.

[0006] To overcome these disadvantages, processes have been proposed in the art for improving the catalytic performances of these zeolitic compounds by appropriate activation treatment.

[0007] For example, the patent U.S. 4,937,216 describes a process for the preparation of epoxides from olefins and hydrogen peroxide which uses, as catalyst, a titanium silicalite treated, before or during the epoxidation reaction, with a neutralizing agent selected from organic derivatives of silicon of the type X-Si$(R)_3$ or hydrosoluble substances deriving from cations of group I and II with a different base strength.

[0008] The patent EP-712.852 discloses an epoxidation process of olefins in the presence of titanium-silicalite which uses as neutralizing agent a non base salt selected from lithium chloride, sodium nitrate, potassium sulfate and ammonium phosphate.

[0009] The patent U.S. 5,675,026 describes an epoxidation process which uses as catalyst a titanium-silicalite treated, before or during the reaction, with a neutral salt or acid, selected from Na_2SO_4, $(NH_4)_2SO_4$, NH_4NO_3 or NaH_2PO_4.

[0010] Operating according to these known processes, propylene oxide is obtained with a good yield and selectivity.

[0011] These processes however have disadvantages deriving from the fact that these catalytic systems have a short duration of the catalytic cycle and consequently require frequent regeneration.

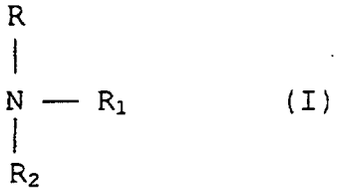
[0012] This creates considerable problems from both a technical and economic point of view, above all when the epoxidation process is carried out in continuous.

[0013] In fact, a lowering in the production yield of the epoxide and a reduction of the catalytic activity have been observed during the subsequent regeneration phases.

[0014] There is therefore the obvious necessity of developing epoxidation processes which allow a high conversion and selectivity to be obtained, simultaneously maintaining the stability of the catalytic activity during the reaction.

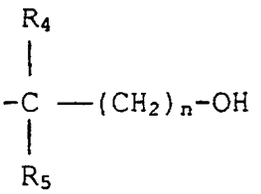
[0015] It has now been found that these requirements can be satisfied if the epoxidation reaction of olefins is carried out in the presence of suitable nitrogenated bases.

[0016] In accordance with this, the present invention relates to a process in continuous for the preparation of olefin oxides by the direct oxidation of an olefin with hydrogen peroxide, or compounds capable of producing hydrogen peroxide under the reaction conditions, in a solvent medium, in the presence of a catalytic system consisting of a synthetic zeolite containing titanium atoms and a nitrogenated base having general formula (I)



(I)

wherein: R, R_1 and R_2, the same or different, can be H, an alkyl group with C_1-C_{10} carbon atoms, or a



group wherein n is a number ranging from 1 to 10 and R_4 and R_5 are H or an alkyl group with C_1-C_{10} carbon atoms, on the condition that R, R_1 and R_2 are not contemporaneously H.

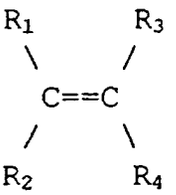
[0017] Preferred compounds having formula (I) are: methylamine, ethylamine, n-propylamine, diethylamine, n-butylamine, ethanolamine, diethanolamine, and triethanolamine.

[0018] The compound having formula (I) is fed in continuous and is present in such a concentration as to neutralize the acidity of the reaction mixture.

[0019] The concentration however of this compound (I) generally ranges from 5 to 500 ppm (by weight) with respect to the reaction mixture, preferably from 10 to 100 ppm.

[0020] The olefin compounds which can be used in the process of the present invention can be selected from organic compounds having at least one double bond and can be aromatic, aliphatic, alkylaromatic, cyclic, branched or linear. They are preferably olefin hydrocarbons having from 2 to 30 carbon atoms in the molecule and containing at least one double bond.

[0021] Examples of olefins suitable for the purposes of the present invention are selected from those having general formula (II)



wherein: R_1, R_2, R_3 and R_4, the same or different, can be H, an alkyl radical with from 1 to 20 carbon atoms, an aryl radical, an alkylaryl radical with from 7 to 20 carbon atoms, a cycloalkyl radical with from 6 to 10 carbon atoms, an alkylcycloalkyl radical with from 7 to 20 carbon atoms. The radicals R_1, R_2, R_3 and R_4, can form, in pairs, saturated or unsaturated rings. These radicals may additionally contain halogen atoms, nitro, nitrile, sulfonic groups and relative esters, carbonyl, hydroxyl, carboxyl, thiol, amine and ether groups.

[0022] Examples of olefins which can be epoxidated with the process of the present invention are: ethylene, propylene, allyl chloride, allyl alcohol, butenes, pentenes, hexenes, octeneheptenes-1, 1-tridecene, mesityl oxide, isoprene, cyclo-octene, cyclohexene or bicyclic compounds such as norbornenes, pinenes, etc.

[0023] The olefins can carry the above substituents both on the unsaturated carbon atoms and on different positions.

[0024] The oxidizing agent used in the process of the present invention is hydrogen peroxide (H_2O_2) or a compound which is capable of generating H_2O_2 under the epoxidation conditions.

[0025] An aqueous solution of hydrogen peroxide is preferably used, at a minimum concentration of 1% by weight, preferably with a titer greater than or equal to 35% by weight.

[0026] The quantity of hydrogen peroxide with respect to the olefin is not critical, but a molar ratio olefin/H_2O_2 ranging from 10:1 to 1:10, preferably from 6:1 to 1:2, is preferably used.

[0027] The epoxidation reaction can be carried out in one or more solvents liquid at the epoxidation temperatures. Solvents of a polar nature are typically used, such as alcohols (methanol, ethanol, isopropyl alcohol, t-butyl alcohol, cyclohexanol), ketones (for example acetone, methyl ethyl ketone, acetophenone), ethers (tetrahydrofuran, butyl ether), aliphatic and aromatic hydrocarbons, halogenated hydrocarbons, esters.

[0028] Methanol and, among the ketones, acetone, are preferably used. A mixture of methanol/water with a weight ratio ranging from 50/50 to 99/1, is particularly preferred.

[0029] The temperatures used in the process of the present invention generally range from 20 to 150°C, preferably from 40 to 100°C. The operating pressures are those which allow the olefin to be maintained in liquid phase at the preset reaction temperature. The operating pressure is generally higher than atmospheric pressure when gaseous olefins are used.

[0030] The catalyst which can be used in the process of the present invention is selected from those generally known

by the name of titanium-silicalites.

[0031] For example titanium-silicalites with an MFI structure can be used, described in the patent U.S. 4,410,501 which also specifies their structural characteristics.

[0032] Titanium-silicalites can also be used, in which part of the titanium is substituted by other metals, such as boron, aluminum, iron or gallium. These substituted titanium silicalites and the methods for their preparation are described in European patent applications 226,257, 226,258 and 266,825.

[0033] It is also possible to use titanium silicalites with a MEL or intermediate MFI/MEL structure described in Belgian patent 1,001,038. Other titanium-silicalites can be selected from beta zeolites containing titanium and having a BEA structure, described in Spanish patent 2,037,596, ZSM-12 containing titanium and optionally aluminum, described in "Journal of Chemical Communications, 1992, page 745).

[0034] The preferred catalyst according to the present invention is titanium-silicalite having the general formula:

$$xTiO_2 \cdot (1-x)SiO_2$$

wherein: x represents a number ranging from 0.0001 to 0.04, preferably from 0.01 to 0.025, and described, for example, in U.S. patents 4,410,501, 4,824,976, 4,666,692, 4,656,016, 4,859,785, 4,937,216.

[0035] The quantity of catalyst used in the process of the present invention is not critical; it is selected however in such a way as to allow the epoxidation reaction to be completed in as short a time as possible.

[0036] The quantity of catalyst is generally selected in relation to various parameters, such as the reaction temperature, the reactivity and concentration of the olefins, the concentration of hydrogen peroxide, the type and composition of the solvent, the catalytic activity and type of reactor or reaction system used.

[0037] The quantity of catalyst typically ranges from 1 to 15% by weight with respect to the reaction mixture and, preferably, from 4 to 10% by weight.

[0038] The catalyst can be used in the form of powder, pellets, microspheres, extruded product or other convenient physical forms.

[0039] The epoxidation process of the present invention can be carried out in batch, semi-continuous or, preferably, in continuous.

[0040] Various types of reactor can be used in the process of the present invention, for example a slurry reactor or a fixed-bed reactor.

[0041] The epoxidation process is preferably carried out in continuous, by feeding into a reaction zone containing the catalyst: the solvent, hydrogen peroxide, the olefin and the compound having general formula (I).

[0042] The epoxide obtained with the process of the present invention can be separated and recovered from the reaction mixture using suitable techniques such as fractionated distillation.

[0043] The following examples have the sole purpose of describing the present invention in greater detail and should in no way be considered as limiting its scope.

Example 1 (comparative)

Oxidation of propylene

[0044] The epoxidation reaction is carried out in a stirred, 1.5 litre, AISI 316L steel reactor, equipped with a thermostat-regulation system, level control, pressure control and filter for continuously removing the solution, maintaining the catalyst in the reactor.

[0045] 760 g of a solution of methanol/water (93/7) and 40 g of titanium silicalite TS-1 (EniChem, with a titanium content equal to 2.05% by weight) are initially charged.

[0046] After thermostat-regulating the system at 60°C and pressurizing with propylene to 12 bar, the following products are fed in continuous by means of pumps:

1. 1970 g/hour of a solution of methanol/water 92.8/7.2 by weight
2. 230 g/hour of an aqueous solution of H_2O_2 at 35% by weight
3. propylene
4. 100 g/hour of water.

[0047] The overall reaction mixture in the feeding (without propylene) is equal to 2300 g/hour and its composition is the following:
H_2O_2 3.5%, H_2O 17%, MeOH 79.5%.
The pressure in the reactor is maintained at 12 bar, feeding propylene.

[0048] The reaction trend is followed by taking samples every two hours and determining the residual H_2O_2 by titration with sodium thiosulfate and the reaction products by gaschromatography.

[0049] The results are indicated in Table 1.

Table 1

Reaction hours	H_2O_2 conversion %	PO selectivity %
6	90	67
16	82	75
30	75	80

Example 2 (comparative)

[0050] The reaction is carried out under the same conditions described in example 1, but feeding in continuous (100 g/hour) an aqueous solution containing 0.115% by weight of sodium acetate, corresponding to 50 ppm of the reaction mixture. The results are indicated in table 2.

Table 2

Reaction hours	H_2O_2 conversion %	PO selectivity %
6	96	84
16	94	91
30	87	96

Example 3 (comparative)

[0051] The same procedure is adopted as in example 1, but feeding in continuous (100 g/hour) an aqueous solution containing 0.092% by weight of $NaNO_3$, corresponding to 40 ppm in the reaction mixture. The results are shown in table 3.

Table 3

Reaction hours	H_2O_2 conversion %	PO selectivity %
6	92	71
16	87	82
30	84	86

Example 4 (comparative)

[0052] The same procedure is adopted as in example 1, but feeding in continuous (100 g/hour) an aqueous solution containing 0.046% by weight of NaOH, corresponding to 20 ppm in the reaction mixture. The results are shown in table 4.

Table 4

Reaction hours	H_2O_2 conversion %	PO selectivity %
6	85	93
16	65	97.5
30	45	98

Example 5

[0053] The same procedure is adopted as in example 1, but feeding (100 g/hour) an aqueous solution containing 0.23% of ethanolamine, corresponding to 100 ppm in the reaction mixture. The results are shown in table 5.

Table 5

Reaction hours	H_2O_2 conversion %	PO selectivity %
6	94	97.5
30	92.5	97.2
40	89	97.4

Example 6

[0054] The same procedure is adopted as in example 1, but feeding (100 g/hour) an aqueous solution containing 0.23% of ethylamine, corresponding to 100 ppm in the reaction mixture. The results are shown in table 6.

Table 6

Reaction hours	H_2O_2 conversion %	PO selectivity %
6	95	96.8
30	92	96.5
40	91	97.5

Example 7

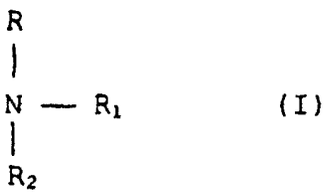
[0055] The same procedure is adopted as in example 1, but feeding (100 g/hour) an aqueous solution containing 0.23% of n-propylamine, corresponding to 100 ppm in the reaction mixture. The results are shown in table 7.

Table 7

Reaction hours	H_2O_2 conversion %	PO selectivity %
6	92	96.5
30	91.5	96.8
40	91.7	97

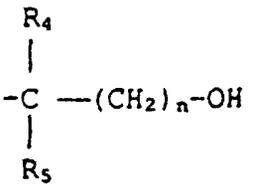
Claims

1. A process in continuous for the preparation of olefin oxides by the direct epoxidation of an olefin with hydrogen peroxide, or compounds capable of producing hydrogen peroxide under the reaction conditions, in a solvent medium, in the presence of a catalytic system consisting of a zeolite containing titanium atoms and a nitrogenated base having general formula (I)



(I)

wherein: R, R_1 and R_2, the same or different, can be H, an alkyl group with C_1-C_{10} carbon atoms, or a



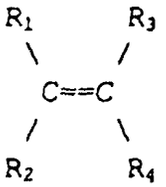
group, wherein n is a number ranging from 1 to 10 and R_4 and R_5 are H or an alkyl group with C_1 -C_{10} carbon atoms, on the condition that R, R_1 and R_2 are not contemporaneously H.

2. The process according to claim 1, wherein the compound having formula (I) is selected from ethylamine, n-propylamine, diethylamine, n-butylamine, ethanolamine, diethanolamine and triethanolamine.

3. The process according to claim 1, wherein the starting olefin compounds are selected from aromatic, aliphatic, alkylaromatic, cyclic, branched or linear organic compounds, having at least one double bond.

4. The process according to claim 3, wherein the olefin compounds are selected from olefin hydrocarbons having from 2 to 30 carbon atoms in the molecule and containing at least one double bond.

5. The process according to claim 4, wherein the olefin compounds are selected from those having general formula (II)



wherein: R_1, R_2, R_3 and R_4, the same or different, can be H, an alkyl radical with from 1 to 20 carbon atoms, an aryl radical, an alkylaryl radical with from 7 to 20 carbon atoms, a cycloalkyl radical with from 6 to 10 carbon atoms, an alkylcycloalkyl radical with from 7 to 20 carbon atoms.

6. The process according to claim 5, wherein the radicals R_1, R_2, R_3 and R_4 can form, in pairs, saturated or unsaturated rings.

7. The process according to claim 4, wherein the radicals R_1, R_2, R_3 and R_4 can contain substituents selected from halogens, nitro, nitrile, sulfonic groups and relative esters, carbonyl, hydroxyl, carboxyl, thiol amine and ether groups.

8. The process according to claim 1, wherein the olefin is propylene.

9. The process according to claim 1, wherein the compound having formula (I) is used in a quantity ranging from 5 to 500 ppm by weight with respect to the reaction mixture.

10. The process according to claim 9, wherein the compound having formula (I) is used in a quantity ranging from 10 to 100 ppm by weight with respect to the reaction mixture.

11. The process according to claim 1, wherein the hydrogen peroxide is used as an aqueous solution with a minimum titer of 1% by weight.

12. The process according to claim 11, wherein the hydrogen peroxide is used as an aqueous solution with a titer equal to or higher than 35% by weight.

13. The process according claim 1, wherein the molar ratio between olefin and hydrogen peroxide ranges from 10/1 to 1/10.

14. The process according claim 13, wherein the molar ratio between olefin and hydrogen peroxide ranges from 6/1 to 1/2.

15. The process according to claim 1, wherein the catalyst is selected from titanium silicalites having the following general formula:

$$xTiO_2 \cdot (1-x)SiO_2$$

wherein: x ranges from 0.0001 to 0.04.

16. The process according to claim 15, wherein the value of x ranges from 0.01 to 0.025

17. The process according to claim 15, wherein in the titanium silicalite part of the titanium is substituted by metals selected from boron, aluminum, iron or gallium.

18. The process according to claim 1, wherein the epoxidation reaction is carried out in one or more solvents, liquid at the epoxidation temperatures, selected from alcohols, ketones, ethers, aliphatic and aromatic hydrocarbons, halogenated hydrocarbons, esters and glycols.

19. The process according to claim 18, wherein the alcohols are selected from methanol, ethanol, isopropyl alcohol, t-butyl alcohol, cyclohexanol.

20. The process according to claim 18, wherein the ketones are selected from acetone, methyl ethyl ketone, acetophenone.

21. The process according to claim 18, wherein the ethers are selected from tetrahydrofuran and butyl ether.

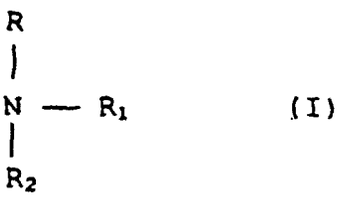
22. The process according to claim 18, wherein the solvent medium is a mixture of methanol/water with a weight ratio ranging from 50/50 and 99/1.

23. The process according to claim 1, wherein the epoxidation reaction is carried out at a temperature ranging from 20 to 150°C.

24. The process according to claim 21, wherein the temperature ranges from 40 to 100°C.

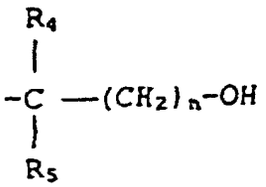
Patentansprüche

1. Kontinuierliches Verfahren zur Herstellung von Olefinoxiden durch die direkte Epoxidation eines Olefins mit Wasserstoffperoxid oder Verbindungen, welche unter den Reaktionsbedingungen Wasserstoffperoxid erzeugen können, in einem Lösungsmittelmedium in Gegenwart eines katalytischen Systems, das aus Zeolithenthaltenden Titanatomen und einer nitrogenierten Base mit der allgemeinen Formel (I)



(I)

besteht, worin R, R_1 und R_2 gleich oder verschieden sind und H, eine Alkylgruppe mit C_1-C_{10} Kohlenstoffatomen, oder eine Gruppe



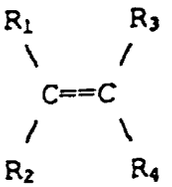
sein können, worin n eine Zahl im Bereich von 1 bis 10 ist und R_4 und R_5 H oder eine Alkylgruppe mit C_1-C_{10} Kohlenstoffatomen sind, unter der Bedingung, dass R, R_1 und R_2 nicht zur gleichen Zeit H sind.

2. Verfahren nach Anspruch 1, worin die Verbindung mit der Formel (I) ausgewählt wird aus Ethylamin, n-Propylamin, Diethylamin, n-Butylamin, Ethanolamin, Diethanolamin und Triethanolamin.

3. Verfahren nach Anspruch 1, worin die Olefinausgangsverbindungen ausgewählt werden aus aromatischen, aliphatischen, alkylaromatischen, zyklischen, verzweigten oder linearen organischen Verbindungen, welche mindestens eine Doppelbindung besitzen.

4. Verfahren nach Anspruch 3, worin die Olefinverbindungen ausgewählt werden aus Olefinkohlenwasserstoffen mit 2 bis 30 Kohlenatoffatomen im Molekül und mit mindestens einer Doppelbindung.

5. Verfahren nach Anspruch 4, worin die Olefinverbindungen ausgewählt werden aus denjenigen mit der allgemeinen Formel (II)



worin R_1, R_2, R_3 und R_4 gleich oder verschieden sind und H, ein Alkylrest mit 1 bis 20 Kohlenstoffatomen, ein Arylrest, ein Aralkylrest mit 7 bis 20 Kohlenstoffatomen, ein Cycloalkylrest mit 6 bis 10 Kohlenstoffatomen, ein Alkylcycloalkylrest mit 7 bis 20 Kohlenstoffatomen sein können.

6. Verfahren nach Anspruch 5, worin die Reste R_1, R_2, R_3 und R_4 in Paaren gesättigte oder ungesättigte Ringe bilden können.

7. Verfahren nach Anspruch 4, worin die Reste R_1, R_2, R_3 und R_4 Substituenten enthalten können, welche ausgewählt werden aus Halogenen, Nitro-, Nitril-, Sulfongruppen und relativen Estern, Carbonyl-, Hydroxyl-, Carboxyl-, Thiol-, Aminund Ethergruppen.

8. Verfahren nach Anspruch 1, worin das Olefin Propylen ist.

9. Verfahren nach Anspruch 1, worin die Verbindung mit der Formel (I) in einer Menge im Bereich von 5 bis 500 ppm bezogen auf das Gewicht im Hinblick auf das Reaktionsgemisch verwendet wird.

10. Verfahren nach Anspruch 9, worin die Verbindung mit der Formel (I) in einer Menge im Bereich von 10 bis 100 ppm bezogen auf das Gewicht im Hinblick auf das Reaktionsgemisch verwendet wird.

11. Verfahren nach Anspruch 1, worin das Wasserstoffperoxid als eine wässrige Lösung mit einem minimalen Titer von 1 Gew.-% verwendet wird.

12. Verfahren nach Anspruch 11, worin das Wasserstoffperoxid als eine wässrige Lösung mit einem Titer gleich oder größer als 35 Gew.-% verwendet wird.

13. Verfahren nach Anspruch 1, worin das Molverhältnis zwischen Olefin und Wasserstoffperoxid in einem Bereich

von 10/1 bis 1/10 liegt.

14. Verfahren nach Anspruch 13, worin das Molverhältnis zwischen Olefin und Wasserstoffperoxid in einem Bereich von 6/1 bis 1/2 liegt.

15. Verfahren nach Anspruch 1, worin der Katalysator ausgewählt wird aus Titansillicaliten mit der folgenden allgemeinen Formel:

$$xTiO_2 \cdot (1-x)SiO_2$$

worin x im Bereich von 0,0001 bis 0,04 liegt.

16. Verfahren nach Anspruch 15, worin der Wert von x im Bereich von 0,01 bis 0,025 liegt.

17. Verfahren nach Anspruch 15, worin im Titansilicalit ein Teil des Titans durch Metalle substituiert ist, ausgewählt aus Bor, Aluminium, Eisen oder Gallium.

18. Verfahren nach Anspruch 1, worin die Epoxidationsreaktion ein einem oder mehreren Lösungsmitteln durchgeführt wird, welche bei Reaktionsbedingungen flüssig sind, ausgewählt aus Alkoholen, Ketonen, Ethern, aliphatischen und aromatischen Kohlenwasserstoffen, halogenierten Kohlenwasserstoffen, Estern und Glykolen.

19. Verfahren nach Anspruch 18, worin die Alkohole ausgewählt werden aus Methanol, Ethanol, Isopropylalkohol, t-Butylalkohol, Cyclohexanol.

20. Verfahren nach Anspruch 18, worin die Ketone ausgewählt werden aus Aceton, Methylethylketon, Acetophenon.

21. Verfahren nach Anspruch 18, worin die Ether ausgewählt werden aus Tetrahydrofuran und Butylether.

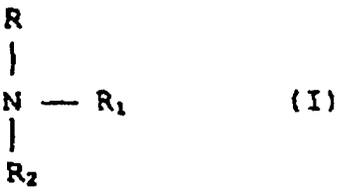
22. Verfahren nach Anspruch 18, worin das Lösungsmittelmedium ein Gemisch aus Methanol/Wasser ist mit einem Gewichtsverhältnis im Bereich von 50/50 bis 99/1.

23. Verfahren nach Anspruch 1, worin die Epoxidationsreaktion bei einer Temperatur im Bereich von 20 bis 150°C durchgeführt wird.

24. Verfahren nach Anspruch 21, worin die Temperatur im Bereich von 40 bis 100°C liegt.

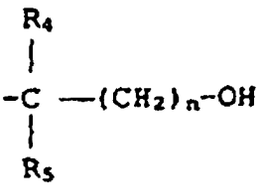
Revendications

1. Procédé en continu pour la préparation d'oxydes d'oléfines par l'époxydation directe d'une oléfine par un peroxyde d'hydrogène, ou des composés capables de produire du peroxyde d'hydrogène sous les conditions de réaction, dans un milieu solvant, en la présence d'un système catalytique consistant en un zéolithe renfermant des atomes de titane et une base azotée ayant pour formule générale (I)



(I)

dans laquelle : R, R_1 et R_2, identiques ou différents, peuvent être un atome H, un groupe alkyle renfermant 1 à 10 atomes de carbone, ou un groupe



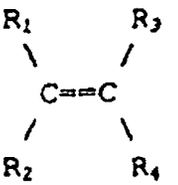
dans lequel n est un nombre de 1 à 10 et R_4 et R_5 sont des atomes d'hydrogène ou un groupe alkyle refermant 1 à 10 atomes de carbone, à la condition que R, R_1 et R_2 ne soient pas simultanément un atome d'hydrogène.

2. Procédé selon la revendication 1, dans lequel le composé ayant pour formule (I) est choisi parmi l'éthylamine, la n-propylamine, la diéthylamine, la n-butylamine, l'éthanolamine, la diéthanolamine et la triéthanolamine.

3. Procédé selon la revendication 1, dans lequel les composés oléfines de départ sont choisis parmi des composés aromatiques, aliphatiques, alkylaromatiques, cycliques, des composés organiques linéaires ou ramifiés, ayant au moins une double liaison.

4. Procédé selon la revendication 3, dans lequel les composés d'oléfines sont choisis parmi des hydrocarbures d'oléfine renfermant 2 à 30 atomes de carbone dans la molécule et ayant au moins une double liaison.

5. Procédé selon la revendication 4, dans lequel les composés oléfines sont choisis parmi ceux ayant pour formule générale (II)



dans laquelle R_1, R_2, R_3 et R_4, identiques ou différents, peuvent être
un atome d'hydrogène, un radical alkyle renfermant 1 à 20 atomes de carbone, un radical aryle, un radical alkylaryle renfermant 7 à 20 atomes de carbone, un radical cycloalkyle renfermant 6 à 10 atomes de carbone, un radical alkylcycloalkyle renfermant 7 à 20 atomes de carbone.

6. Procédé selon la revendication 5, dans lequel les radicaux R_1, R_2, R_3 et R_4 peuvent former, par paire, des cycles saturés ou insaturés.

7. Procédé selon la revendication 4, dans lequel les radicaux R_1, R_2, R_3 et R_4 peuvent refermer des substituants choisis parmi les halogènes, les groupes sulfoniques, nitriles, nitro, et les esters relatifs, les groupes carbonyle, hydroxyle, carboxyle, thiol, amine et éther.

8. Procédé selon la revendication 1, dans lequel l'oléfine est un propylène.

9. Procédé selon la revendication 1, dans lequel le composé ayant la formule (I) est utilisé dans une quantité s'étendant de 5 à 500 ppm en poids par rapport au mélange réactionnel.

10. Procédé selon la revendication 9, dans lequel le composé ayant la formule (I) est utilisé dans une quantité s'étendant de 10 à 100 ppm en poids par rapport au mélange réactionnel.

11. Procédé selon la revendication 1, dans lequel le peroxyde d'hydrogène est utilisé comme une solution aqueuse avec un titre minimum de 1% en poids.

12. Procédé selon la revendication 11, dans lequel le peroxyde d'hydrogène est utilisé comme une solution aqueuse avec un titre égal ou supérieur à 35% en poids.

13. Procédé selon la revendication 1, dans lequel le rapport molaire entre l'oléfine et le peroxyde d'hydrogène s'étend de 10/1 à 1/10.

14. Procédé selon la revendication 13, dans lequel le rapport molaire entre l'oléfine et le peroxyde d'hydrogène s'étend de 6/1 à 1/2.

15. Procédé selon la revendication 1, dans lequel le catalyseur est choisi parmi des silicalites au titane ayant la formule générale suivante :

$$xTiO_2 \cdot (1-x)SiO_2$$

dans laquelle x s'étend de 0,0001 à 0,04

16. Procédé selon la revendication 15, dans lequel la valeur de x s'étend de 0,01 à 0,025.

17. Procédé selon la revendication 15, dans lequel la partie silicalite au titane du titane est substituée par des métaux choisis parmi le bore, l'aluminium, le fer ou le gallium.

18. Procédé selon la revendication 1, dans lequel la réaction d'époxydation est effectuée dans un ou plusieurs solvants, liquides aux températures d'époxydation, choisis parmi des alcools, des cétones, des hydrocarbures aliphatiques et aromatiques, des hydrocarbures halogénés, des éthers et des glycols.

19. Procédé selon la revendication 18, dans lequel les alcools sont choisis parmi le méthanol, l'éthanol, l'alcool isopropylique, l'alcool t-butylique, le cyclohexanol.

20. Procédé selon la revendication 18, dans lequel les cétones sont choisies parmi l'acétone, la méthyléthylcétone, l'acétophénone.

21. Procédé selon la revendication 18, dans lequel les éthers sont choisis parmi le tétrahydrofuranne et l'éther butylique.

22. Procédé selon la revendication 18, dans lequel le milieu solvant est un mélange méthanol / eau avec un rapport pondéral s'étendant de 50/50 à 99/1.

23. Procédé selon la revendication 1, dans lequel la réaction d'époxydation est effectuée à une température s'étendant de 20 à 150°C.

24. Procédé selon la revendication 21, dans lequel la température s'étend de 40 à 100°C.